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Electron Spin Resonance Study on Radical Anions of Acridine and Its Halogen Derivatives

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ESR spectra of radical anions produced by bringing 9-chloro-, 2,7-dibromo-9-chloro-, and 2,4,5,7-tetrabromo-9-chloroacridine into contact with alkali metal (sodium and potassium) in tetrahydrofuran were measured at room temperature and/or at lower temperatures, and the analysis of them was made by means of a simulation method. Hyperfine coupling constants of acridine anion radicals, produced by the similar method in tetrahydrofuran and also by the electrolytic reduction in acetonitrile with the flow method, were determined, taking those of halogen derivatives into consideration. ESR spectra of acridine and 9-chloroacridine anion radical were found to involve the coupling of sodium, showing that these radicals were in the form of ion pair. The coupling constants of bromoacridine anion radicals did not give any difference between the sodium and the potassium reduction. The couplings of halogen atoms were not observed. Good agreement was obtained between the coupling constants calculated from spin densities and those determined experimentally. In general, the solution of radical anions of halogenides gradually yields brownish aggregates at lower temperatures ($-20\sim-30$°C), their ESR spectra becoming weaker and unresolved. The temperature change is reversible and qualitatively resembles the behavior of acridine anion radical.

In a previous paper,[1] the physicochemical behavior of the radical anions of acridine paired with alkali cations in THF was investigated in detail. It was found that the paramagnetic monovalent anion transforms to the diamagnetic dianion in the presence of excess alkali metal and that a certain association reaction of the $n(A^-Na^+)\rightleftharpoons(A^-Na^+)_n$ type (n, perhaps 2) occurs in THF. It was further found that this equilibrium shifts to right with lowering the temperature. Furthermore, we obtained the ESR spectrum consisting of more than fifty lines most plausibly attributable to the radical anion of acridine, but an attempt for analysis was postponed.

When we succeeded in taking the ESR spectrum with hyperfine structure, there was no such work found in literature. But in the course of our investigation, two papers dealing with the ESR of acridine radical anion appeared. One is Hoeve and Yeranos's[2] and the other, Szwarc *et al.*'s.[3] The hfs constants of the acridine radical anion produced by electrolysis in pyridine were determined by the former workers, while by the latter workers the similar determination was made for the radical anion produced by the alkali metal method in hexamethylphosphoramide.

In continuance of our study we have succeeded in obtaining the ESR spectrum of acridine radical anion produced electrolytically in acetonitrile. Although the radical anion thus produced was rather unstable, its hfs could be studied successfully by employing the flow method. Further, we have taken the ESR spectra of radical anions originating from a few halogen substituted acridines which also displayed good hfs. As is well known, the substitution of halogen atoms for aromatic ring protons generally makes the analysis of the spectrum easier because of the disappearance of the proton coupling[4] at the substitution positions (there is some line broadening, however, and in the case of chlorine substitution there are some papers reporting on the resolution of hfs coupling of chlorine,[5,6] which is rather remarkable).

The results for the radical anions of (I) have been found to be in good agreement with those in literature except for the case of sodium reduction, in which the sodium coupling was observed and other coupling constants were somewhat different from those in other cases. This implies that the radical anion in the latter cases exists

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[1] S. Niizuma, M. Okuda and M. Koizumi, This Bulletin, **41**, 795 (1968).

[2] H. G. Hoeve and W. A. Yeranos, *Mol. Phys.*, **12**, 597 (1967).

[3] J. Chandhuri, S. Kume, J. Jagur-Grodzinski and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 6421 (1968).

[4] M. Bruin, F. Bruin and F. W. Heineken, *J. Chem. Phys.*, **37**, 135 (1962).

[5] T. C. Hollocher, N. M. Tooney and R. Adman, *Nature*, **197**, 74 (1963).

[6] B. T. Allen and W. Vanneste, *ibid.*, **204**, 991 (1964).

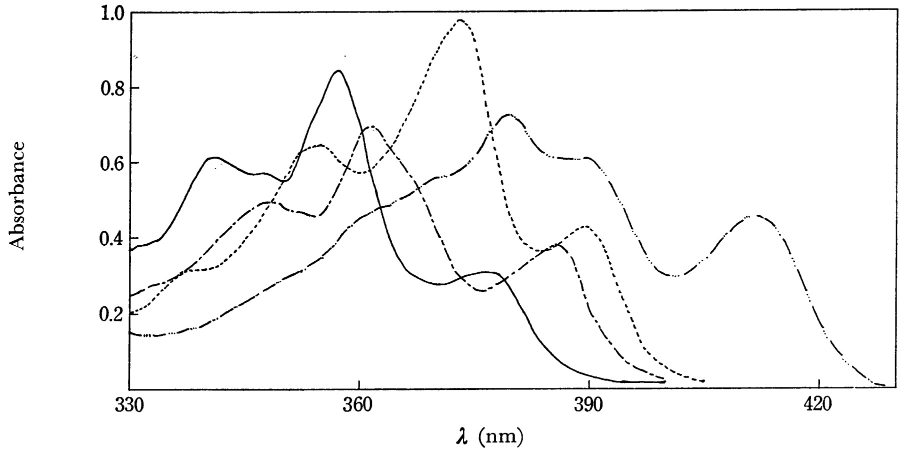
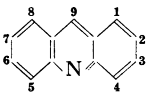
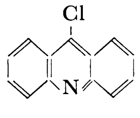


Fig. 1. Electronic absorption spectra of acridine and its halogen derivatives. *ca.* 7×10^{-5} M in tetrahyrofuran.
——; I, —·—; II, ----; III, —···—; IV

essentially as free (at least from the viewpoint of ESR) while with sodium cation the formation of ion pair occurs. It has been established that the coupling constants obtained, satisfy McConnell's relation moderately well.



(I)



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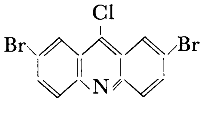

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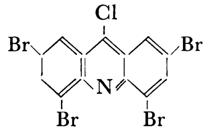

(IV)

Experimental

A JEOL P-10 type ESR spectrometer was used. Its characteristics and the apparatus for temperature control are the same as descrived in the previous paper.[1]

Materials. THF was purified in the same way as in the previous paper.[1] First grade acetonitrile from Wako Junyaku was distilled, dried on calciumhydride and then stored in vacuo. (I) was purified in the way described in the previous paper.[7] (II) was synthesized from *N*-phenylanthranylic acid after Albert and Ritchie,[8] (III) and (IV) from acridon after Acheson and Robinson[9] and recrystalized from THF. Mass spectra of these halogenides were in good agreement with the theoretical distribution. Electronic spectra of these compounds are shown in Fig. 1.

Procedure. Anion radicals were prepared by bringing 2 m*l* degassed THF solutions containing several mg of acridines into contact with a sodium mirror deposited by vacuum evapolation. In the case that an anion was unstable at room temperature, the contact was carried out in dry ice methanol bath. A flow method apparatus as shown in Fig. 2 was devised for the steady current electrolysis. The flow was controlled by cock C, and checked by the time interval necessary for one drop to fall down from the tip of capillary, F. The optimum flow rate was 10.3 sec/one drop. 5 to 6 V was applied between anode and cathod, A and B.

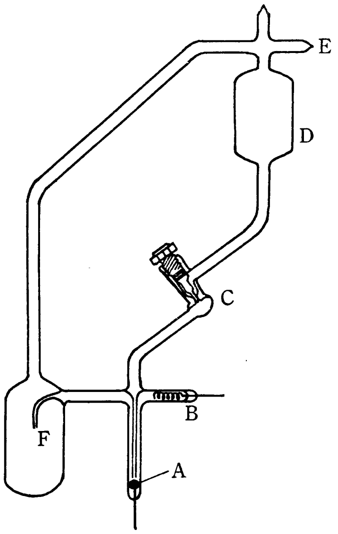

Fig. 2. The apparatus for the flow method electrolytic reduction.
A; Mercury anode
B; Platinum cathode
C; Teflon greeseless cock
D; Reservoir for the solution
E; A diffusion pump
F; Capillary for checking the flow rate

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[7] S. Niizuma and M. Koizumi, This Bulletin, **36**, 1629 (1963).

[8] Albert and Ritchie, *Org. Synthesis*, **22**, 5 (1942).

[9] R. M. Acheson and M. J. T. Robinson, *J. Chem. Soc.*, **1954**, 232; *ibid.*, **1953**, 4142.

Spin Density Calculation and Simulation of ESR Spectrum. The spin densities on nitrogen, carbon and halogen atoms of acridines were calculated by a simple LCAO-MO method. For simulation of ESR spectra, the simulation program was composed in our laboratory. The calculation and the simulation were carried out on the NEAC-2200 Model 500 Electronic Computer in the Calculation Center of Tohoku University.

Results and Discussion

2,4,5,7-Tetrabromo-9-chloroacridine (IV). ESR spectrum obtained by making contact with sodium mirror at room temperature, is shown in Fig. 3(a). The spectrum changes from (a) to (d) as the temperature is lowered and this temperature change is reversible. It is seen that the signal is more resolved at lower temperature, and at room temperature it becomes highly broadened with no apparent reduction in intensity. Any difference was not observed between sodium and potassium as a reducing agent. This means that the two anion radicals have the similar structures, suggesting that they exist as free ions. But these two ion pairs which are equally unstable at room temperature show quite different modes of destruction. Thus the ion pair with sodium cation decays according to the first order rate formula with a half life of 180 min (at 22°C) while the potassium ion pair obeys the second order (Fig. 4a, b). Furthermore the solution after reaction becomes yellowish brown in the former case while in the latter it is colorless and the electronic absorption spectrum strongly suggests the destruction of acridine frame.

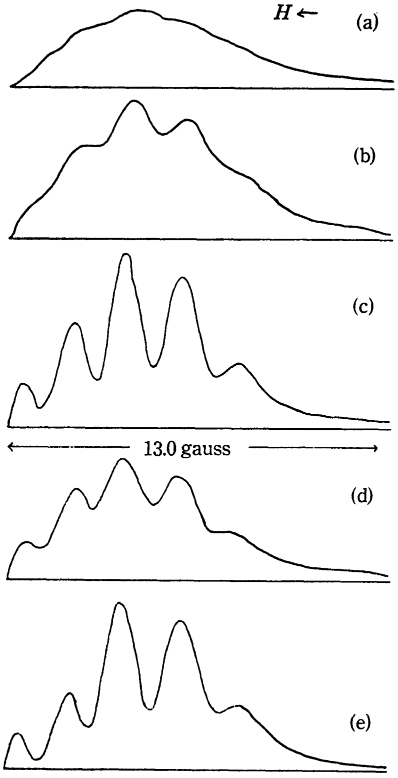

Fig. 3. ESR spectra of radical anion of IV. (a); at +15°C, (b); at −16°C, (c); at −55°C, (d); at −70°C, (e); Simulated spectrum, corresponding to (c).

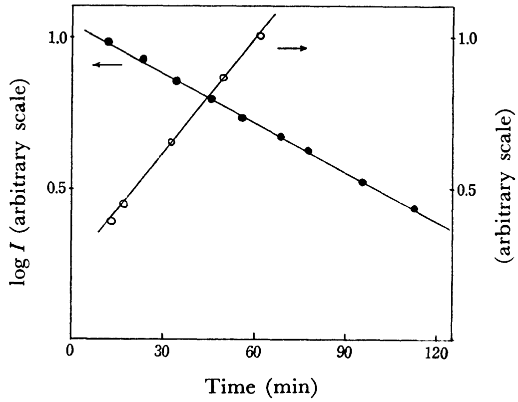

Fig. 4. The decay curve of ESR signal intensity for radical anion of IV.
● Sodium reduction, at 22°C
○ Potassium reduction, at 0°C

By assuming that the coupling of halogen atoms is not resolved and by neglecting the coupling of sodium, hfs was analysed satisfactorily. The simulation spectrum obtained by taking only a nitrogen atom and two pairs of magnetically equivalent protons, is shown in Fig. 3(e) which corresponds to the observed one (c). The parameters used for simulation and the calculated spin densities are listed respectively in Tables 1 and 2 given later, together with those for the other compounds.

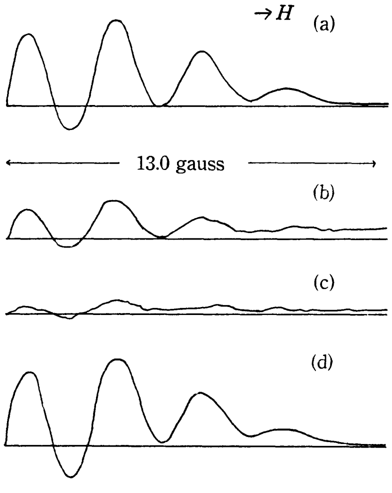

Fig. 5. ESR spectra of radical anion of III. (a) at +22°C, (b) at −51°C, (c) at −78°C, (d) Simulated spectrum, corresponding to (a).

TABLE 1.

Anion radical	Method of reduction	Temp.	Coupling constant (gauss)							Δh (gauss)	Total width (gauss)
			H_1	H_2	H_3	H_4	H_9	N	Metal		
Acridine	Sodium (THF)	room temp.	2.59	1.13	2.14	2.03	8.78	4.17	0.56	0.10	34.6
	Potassium (THF)	room temp.	2.83	0.57	2.31	1.36	7.74	3.79		0.34	29.5
	Electrolytic (CH_3CN)	room temp.	2.75	0.79	2.23	1.57	7.60	3.40	—	0.34	29.1
	Electrolytic[2] (pyridine)	10°C	2.73	0.81	2.19	1.60	7.74	3.48	—		29.4
	Sodium[3] (HMPA)	room temp.	2.78	0.91	2.02	1.82	7.60	3.72			30.1
	Calcd*		2.65	0.75	1.90	1.60	7.60	3.60			28.6
9-Chloro-acridine	Sodium (THF)	−55°C	2.90	0.80	2.30	1.60	—	3.90	0.80	0.60	25.4
	Calcd*		2.71	0.64	1.93	1.56	—	3.24			20.2
2,7-Dibromo-9-chloro-acridine	Sodium and potassium (THF)	room temp.	3.00	—	2.60	0.87	—	3.10		1.00	19.1
	Calcd*		2.48	—	2.04	1.59	—	3.37			19.0
2,4,5,7-Tetra-bromo-9-chloroac-ridine	Sodium (THF)	−55°C	2.20	—	2.00	—	—	3.42		1.45	15.2
	Potassium (THF)	−58°C									
	Calcd*		2.23	—	1.76	—	—	3.62			15.2

* The values calculated by a simple LCAO-MO method (see text).

TABLE 2. UNPAIRED SPIN DENSITY

Compound	C_1	C_2	C_3	C_4	C_9	N	C_N*
Acridine	0.0947	0.0268	0.0679	0.0570	0.2716	0.1507	0.0368
9-Chloroacridine	0.0969	0.0229	0.0690	0.0558	(0.2648)**	0.1338	0.0377
2,7-Dibromo-9-chloroacridine	0.0886	(0.0225)	0.0729	0.0569	(0.2569)	0.1391	0.0368
2,4,5,7-Tetrabromo-9-chloroacridine	0.0795	(0.0237)	0.0629	(0.0579)	(0.2440)	0.1495	0.0408

* C_N carbon atom adjacent to nitrogen.

** The value in the parenthesis is the spin density at the position substituted by halogen.

2,7-Dibromo-9-chloroacridine (III). The radical anion originating from this compound has four sets of atoms which are responsible for hfs, *i.e.*, a nitrogen and three pairs of magnetically equivalent protons. The anion radical produced from III by using sodium as a reducing agent was stable at room temperature and gave a ESR spectrum shown in Fig. 5(a). Signal intensity decreased with lowering temperature, as is shown in in Fig. 5(b) and (c). This change was reversible and qualitatively the same as observed in the acridine radical anion.[1] The similar ESR signal was obtained by using potassium as a reducing agent and the values of hfs constants were equal to the ones for the sodium reduction. The simulated spectrum, (d) in Fig. 5, corresponds to the observed one, (a) in Fig. 5.

9-Chloroacridine (II). The anion radicals of II were stable at room temperature. Their ESR spectra were measured in the best condition at −55°C for the sodium reduction and at −66°C for the potassium reduction and are shown in Fig. 6(a) and (b) respectively. The analysis of the spectrum for the sodium reduction was accomplished by taking account of sodium coupling, 0.80 gauss as shown in Fig. 6(c). It may be due to the absence of metal coupling that the ESR spectrum for the potassium reduction differs from that for the sodium reduction.

By the prolonged contact with alkali metal, the THF solution of II turned red and ESR signal disappeared. This diamagnetic species is considered to be a dianion by analogy with I.

Acridine (I). ESR spectra of anion radicals

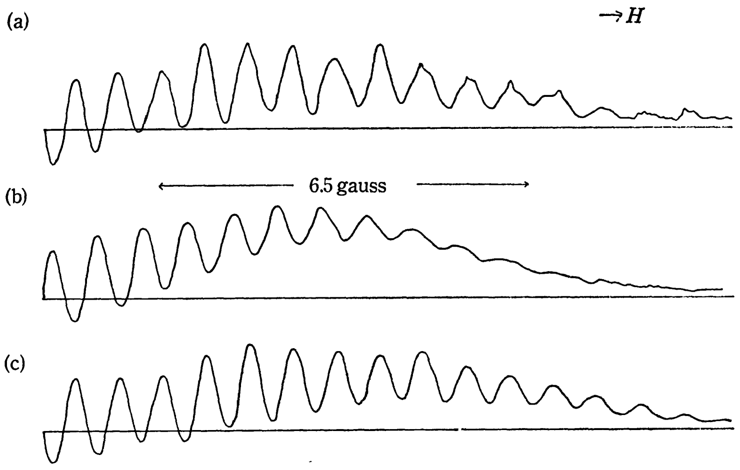

Fig. 6. ESR spectra of radical anions of II.
(a) Sodium reduction, at −55°C
(b) Potassium reduction, at −66°C
(c) Simulated spectrum, corresponding to (a)

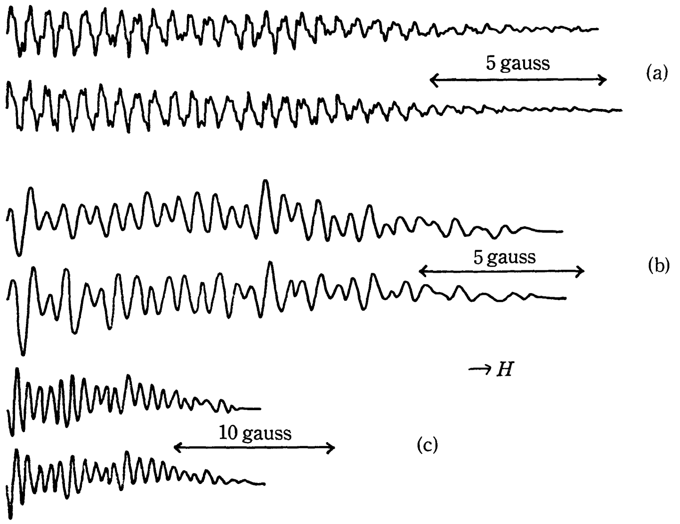

Fig. 7. ESR spectra of radical anions of I.
(a) Sodium reduction, (b) Potassium reduction (c) Electrolytic reduction
For each the upper spectrum; observed, the lower; simulated.

produced from I with the sodium reduction and with the potassium reduction, although they were already given in the previous paper,1) are shown again in Fig. 7 in order to make a comparison with the simulated spectra and with the spectrum of the anion produced by electrolytic reduction.

The anion radical produced by electrolysis of the acetonitrile solution of I was so unstable that we could not make the ESR measurement under the static condition. In the initial stage of electrolysis, the green layer appeared in the solution close to the anode surface, but in several minutes after electrolysis the solution turned pink and proved to be diamagnetic. Therefore we had to use the technique of flow method. By employing the apparatus shown in Fig. 2 and by electrolyzing the acetonitrile solution containing $\sim$1 mM acridine and 30 mM tetra-*n*-propyl ammonium perchlorate we could obtain the ESR spectrum which is shown in Fig. 7.

From Fig. 7 it is evident that only for the sodium reduction, there exists the effect of counter ion (metal cation) on the ESR spectrum. The hfs constant was determined to be 0.56 guass. In spite of the difference in solvent, coupling constants for the potassium reduction are in good agreement with the ones for the electrolytic reduction. Only the values for the sodium reduction are different, and this is certainly due to the formation of ion pair.

The parameters which correspond to the coupling constants and line widths used are listed in Table 1. These values are reliable within ±0.05 gauss. The assignment was made by taking the spin density from a molecular orbital calculation into consideration. The data in Table 2 are electron densities of the lowest vacant orbital for the four compounds under consideration. In the calculation according to the simple LCAO-MO method, the values of the Coulombic integrals and of the resonance integrals were assumed as follows:

$$\alpha_N = \alpha + 0.7\beta, \quad \alpha_{C'-N} = \alpha + 0.1\beta, \quad \beta_{C-N} = \beta$$

$$\alpha_{Cl} = \alpha + 1.8\beta, \quad \alpha_{C'-Cl} = \alpha + 0.18\beta, \quad \beta_{C-Cl} = 0.8\beta$$

$$\alpha_{Br} = \alpha + 1.4\beta, \quad \alpha_{C'-Br} = \alpha + 0.14\beta, \quad \beta_{C-Br} = 0.7\beta$$

α and β are the Coulombic integral of carbon atom and the resonance integral of the C–C bond respectively. The subscripts N, Cl and Br imply the values for nitrogen, chlorine and bromine atom, C′-N *etc.* for carbon atom connecting with nitrogen atom *etc.*, and C–N *etc.* for C–N bond etc.

Spin densities (given in Table 2) *vs.* hfs constants (given in Table 1) are plotted in Fig. 8 to give a linear relation. From its slope, the McConnell's Q-value is obtained as 28 gauss. The coupling constant of nitrogen, a_N was calculated from the following equation,

$$a_N = Q_N \rho_N + \sum Q_{C_i} \rho_{C_i}$$

where ρ_N and ρ_{C_i} are the unpaired spin density on nitrogen and carbon atoms adjacent to nitrogen, C_i. As the values of Q_N and Q_{C_i}, 20 gauss and 7 gauss were used, which had been proposed by Smid.[10]

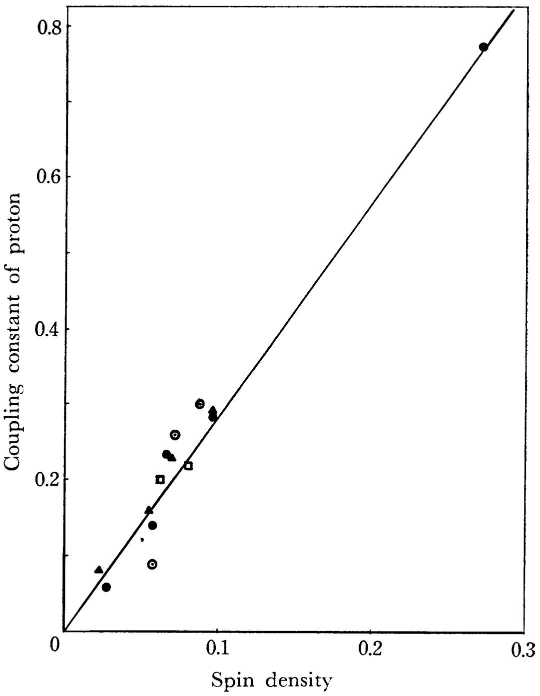

Fig. 8. Plot of spin densities *vs.* hfs constants of protons.
● I (Potassium reduction)
▲ II (Sodium reduction)
⊙ III (Sodium and potassium reduction)
□ IV (Sodium and potassium reduction)

The authors wish to thank Mr. Katubumi Kumano and Mr. Katsumi Nakamaru for supplying the samples.

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[10] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).